

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.76–127

FORMATION OF OPEN POROSITY MATERIALS BASED ON NICKEL, ALUMINUM AND COBALT IN SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS IN VACUUM

V. I. Uvarov,^{1,3} I. P. Borovinskaya,¹ and E. S. Lukin²

Translated from *Steklo i Keramika*, No. 1, pp. 20 – 23, January, 2013.

As a result of a calculation of the influence of the volume effect of a chemical reaction on the porosity of the final product for the system Al–Ni–Co in vacuum it is shown that the porosity of the synthesized material will be 7.6% higher than the initial porosity P_0 of the starting sample. For synthesis of SHS material with open porosity the initial batch powders were mixed in a ball mill with Al_2O_3 balls for 1 h. The ready batch was poured into a graphite mold, which was placed into a vacuum furnace, and the batch temperature was raised to the self-inflammation temperature, after which spontaneous combustion of the batch occurred. Phase analysis of the samples, performed with a DRON-3M diffractometer, showed the presence of the main phase $(\text{CoNi})_3\text{Ni}$ and free Ni. The pore size of the samples obtained was 2 – 2.5 μm . The open porosity of the samples, determined by hydrostatic weighing, was 42%.

Key words: open and closed porosity of materials, microstructure, temperature, combustion, method of self-propagating high-temperature synthesis (SHS).

On porous membranes modified by highly disperse catalytic systems, methane carbon dioxide reforming (MCDR) into syngas proceeds intensively at temperatures 200 – 400°C lower than with processes realized in a conventional flow reactor. With selectivity to syngas it approaches 98% [1 – 3].

The present work is devoted to the synthesis of high-porosity corrosion-resistant membranes for steam conversion of ethanol and glycerin as the main products of the fermentation of biomass into syngas. The search for new materials for ceramic membranes is dictated by the improvement of their effectiveness and performance properties (long service life at high temperatures in aggressive processes). It is also known that the boiling temperature of metals in vacuum approaches the melting temperature of these metals, and the evaporation rate of these metals is 2 – 3 orders of magnitude higher than

the diffusion rate of the metal vapors at external pressure 0.1 MPa. These conditions determine the mechanism by which highly porous materials are formed. In the combustion wave of high-temperature self-propagating synthesis (SHS) the metal in the batch melts and spreads with a liquid interlayer being formed. A number of authors have asserted that the formation of open porosity is mainly due to the filtration of impurity gases, formed in the SHS process, through the liquid phase of the synthesized product [4 – 9]. However, the pressure of the surrounding medium within wide limits was neglected in the analysis of the mechanism of formation of open and closed porosity, and the vapor pressure of the liquid phase of different materials can reach tens of atmospheres during SHS [10, 11]. Likewise, the conditions under which the closed porosity of the synthesized materials can transform into open porosity were not studied.

PRELIMINARY CALCULATIONS

The influence of a change in the specific volume effect of materials in the presence of a chemical reaction on the po-

¹ Federal State Institute of Science – Institute of Structural Micro-kinetics and Materials Science of the Russian Academy of Sciences (ISMAN), Chernogolovka, Russia.

² D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia.

³ E-mail: uvar@ism.ac.ru.

rosity of the final product was calculated first. The calculation was performed using the relation

$$P_f = P_o + (1 - P_o)\Delta, \quad (1)$$

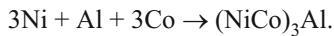
where P_f is the porosity of the synthesized product; $\Delta = (\rho_{f\max} - \rho_{o\max})/\rho_{f\max}$ is the change in the specific volume effect of the materials during a chemical reaction; $\rho_{f\max}$ is the theoretical density of the synthesized product; and, $\rho_{o\max}$ is the maximum density to which the initial batch was pressed with the porosity of the compact going to zero.

Since $\rho_{f\max}$ is tabulated and $\rho_{o\max}$ can also be easily calculated, provided that the composition of the initial batch is known from the prescribed experimental conditions, the parameter Δ can be calculated theoretically for any SHS system. It should be noted that the relation (1) holds only for the synthesis of materials in a closed molding die, when the porosity P_f of the synthesized product depends on the initial porosity P_o of the sample and the volume effect of the materials during the chemical reaction. Swelling of the synthesized sample due to the vapor pressure p_v of the liquid phase and the pressure p_g of the impurity gases formed in the course of the chemical reaction is limited by the size of the molding die.

The dependence of the initial porosity P_o of the sample on the specific compaction pressure p was calculated using A. S. Berezhnoi's relation

$$P_o = a - b \log p,$$

where a and b are empirically determined constants characterizing the rheological properties of a given mix [12]. The constants a and b for a given batch composition were determined from preliminary experiments. The calculation was performed for the reaction



As a result the following values were obtained: $a = 0.34$, $b = 0.064$ at $p = 15$ MPa and $\Delta = 0.127$. This shows that the porosity of the synthesized material will be 7.6% higher than P_o of the initial sample.

The pore size of the synthesized material was also determined. It was calculated using the Laplace relation for a model with cylindrical pores and following GOST 26849–96 (method for determining pore size). The maximum pore size was calculated from the relation

$$2\pi R\sigma \cos \theta = \pi R^2 (\Delta p - h\gamma g),$$

where R is the capillary radius, σ the surface tension of the liquid, θ the wetting angle, h the height of the liquid column above the surface of the sample, γ the density of the liquid, g the acceleration of gravity, $\Delta p = (p_\infty - p_g - p_v)$ the pressure of the gas phase during pore formation, p_∞ the pressure in the

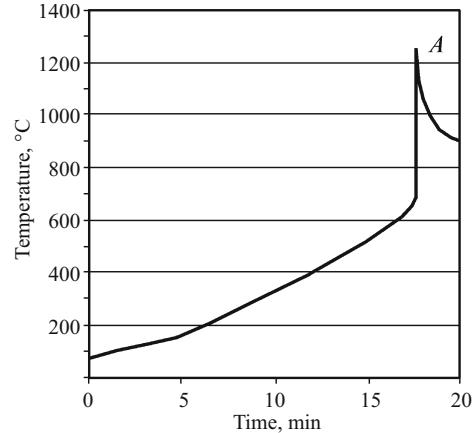


Fig. 1. Variation of the batch temperature in the synthesis regime for samples from Ni–Co–Al.

experimental chamber, p_g the pressure of impurity gases and p_v the vapor pressure of the liquid phase.

The combustion parameters of the SHS system Ni–Al–Co were substituted into the relation for determining the size of open pores: $T_g = 1580$ K and the surface tension of aluminum $s = 0.1116$ N/m [12]. The external pressure p_∞ was 13.3 Pa (0.1 mm Hg); this was the pressure in the experimental chamber. The average pressure p_v of the impurity gases for the system Ni–Al–Co was determined to be 0.5 MPa and the vapor pressure p_v of the liquid phase for aluminum 0.24 MPa [13–15]. As a result of the calculation the critical pore size of the synthesized sample was found to be 2.98 μm .

EXPERIMENTAL STUDIES

The SHS method for synthesizing material with open porosity for the system Ni–Al–Co was also studied experimentally. Since the presence of through pores (i.e., no closed porosity) is the main criterion for filters obtained by the SHS method, it is desirable to synthesize porous material not by layer-wise combustion, as is characteristic for SHS, but rather in the thermal explosion regime. In the present studies the following were used for the system Ni–Al–Co: PN-1 Ni with average particle size 50 μm (43.5%), ASD-4 aluminum powder (13%) and PK-1 cobalt powder (43.5%). The powders were mixed in a ball mill with Al_2O_3 balls for 1 h. The ready batch was poured into a graphite molding die, compacted under pressure $p = 15$ MPa, tightly closed and placed into a vacuum furnace, the temperature was raised to the self-inflammation temperature, and spontaneous combustion of the batch occurred. The regime for the system Ni–Al–Co, where the point A characterizes the completion of the thermal explosion process, is presented in Fig. 1.

The microstructure of fracture of the sample obtained on the basis of Ni–Al–Co presumably in the form of small, hollow, communicating spheres is presented in Fig. 2. The dark

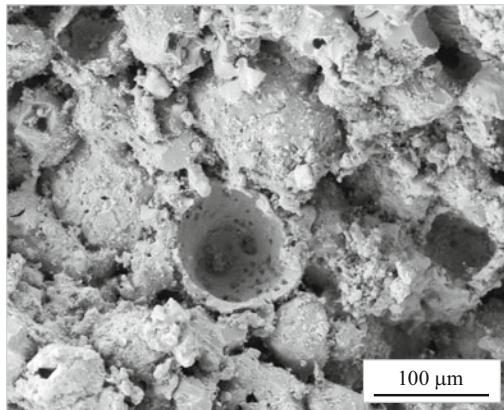


Fig. 2. Microstructure of the fracture of the synthesized sample.

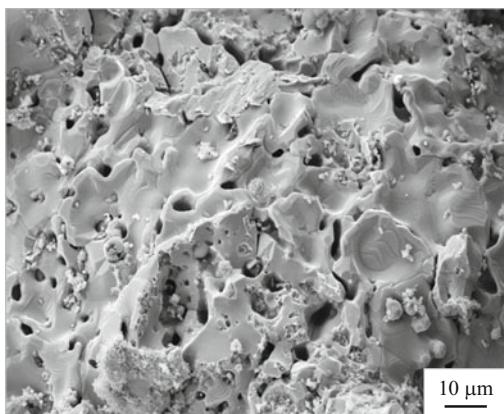


Fig. 3. Microstructure of a part of the surface of an individual hollow sphere permeated by 2–3 μm open pores.

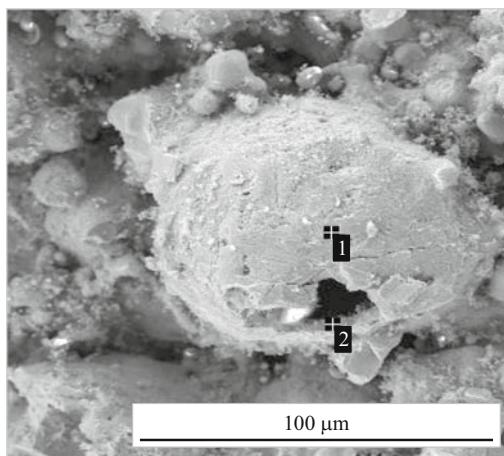


Fig. 4. Microstructure of a sample with elemental analysis at the points 1 and 2 (see Table 1).

spots in the figure indicate the roughness of the fracture surface, irregularities and remnants of closed pores. The size of the open pores (equivalent hydraulic diameter of the channel

TABLE 1. Spectrum of Elemental Analysis of the Fracture of a Sample

Points*	Content of elements at the points studied, wt.%				
	O	Al	Co	Ni	Total
1	2.10	14.41	12.44	71.05	100
2	40.53	37.33	3.39	18.76	100

* See Fig. 4.

along which gas or liquid moves) was measured following GOST 26849–86.

The measurements showed that the pore size of the samples of ceramic membranes obtained was 2–2.5 μm. The open porosity of the samples, determined by hydrostatic weighing, was 42%. A phase analysis of the samples performed with a DRON-3M diffractometer showed the presence of the main phase $(\text{CoNi})_3\text{Al}$ and a very small amount of free Ni.

The microstructure of part of the surface of an individual hollow sphere, permeated with 2–3 μm open pores, is shown in Fig. 3.

The spectrum of an elemental analysis of a fracture of the sample, shown in Fig. 4, is presented in Table 1.

The inner surface of the membrane channels was modified by catalytically active components using the alkoxo method, where the mother liquor solutions of metal-complex precursors were pumped through a membrane attached to a vacuum pump. Next, moist heated air was blown through the membrane, the membrane was dried in vacuum (1 Torr, i.e., 7.5006×10^{-3} Pa) and heated in different regimes. On the basis of the studies (performed jointly with the A. V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences) a catalytic module for steam conversion of ethanol and glycerin as basic products of biomass fermentation into syngas was developed from the synthesized membrane-catalytic system, containing as the active component [La–Ce].

The studies showed that the process of steam conversion of ethanol and glycerin into syngas and hydrogen in catalytic microchannels of ceramic membranes (synergetic effect) occurs with substrate conversion to 90% at 600°C. The specific activity in the formation of hydrogen per hour is 3600 liters/dm³ of the membrane.

CONCLUSIONS

A mechanism for the formation of open porosity in high-temperature, corrosion-resistant, mechanically strong, nanoporous structures based on the system Ni–Al–Co under conditions permitting combustion of batch by SHS in the presence of a liquid phase, impurity gas pressure and liquid-phase vapor pressure was examined. The external pressure was the vacuum.

Phase analysis of the samples showed the presence of the base phase $(\text{CoNi})_3\text{Al}$ and free Ni. The pore size in the membranes prepared was determined following GOST 26849–86 was $2 - 2.5 \mu\text{m}$, which correlates with the computed value ($2.98 \mu\text{m}$). The open porosity in the samples, determined by hydrostatic weighing, was 42%. The permeability of the samples in air was up to 600 liters/(MPa · h).

The process of steam conversion of ethanol and glycerin into syngas and hydrogen in catalytic microchannels of ceramic membranes (synergetic effect) occurs with substrate conversion to 90% at 600°C . The specific activity in hydrogen formation is 3600 liters/dm³ of membrane.

REFERENCES

1. A. Fedotov, V. Zhmakin, M. Tsodikov, and I. Moiseev, "Ceramic membranes in the processes of vapor conversion of ethanol and acetic acid as the main products of biomass fermentation," in: *Utilization of Biomass for Sustainable Fuels and Chemicals (UBIOCHEM): First Workshop of COST Action CM0903*, Cordova, Spain, May 13 – 15, 2010, Cordova (2010), p. 25.
2. M. V. Tsodikov, A. S. Fedotov, V. V. Zhmakin, et al., "Alcohol carbon dioxide reforming using porous membrane-catalytic systems," *Membrany Membrannye Tekhnol.*, No. 1 – 2, 1 – 10 (2011).
3. A. A. Khasin, "New approaches to the organization of the Fisher-Tropsh synthesis process," *Zh. Ross. Khim. Obshch. im. D. I. Mendeleva*, **47**(69), 36 – 47 (2003).
4. A. P. Amosov, A. G. Merzhanov, and I. P. Borovinskaya, *Powder Technology of Self-Propagating High-Temperature Synthesis of Materials* [in Russian], Mashinostroenie-1, Moscow (2007).
5. V. N. Bloshenko, V. A. Bokii, V. I. Boyarchenko, et al., "Titanium oxide based Porous materials obtained in the combustion regime," in: *Abstracts of Reports at the 2nd All-Union Symposium on Advanced Metallic Materials, May 12 – 17 May 1991* [in Russian], Moscow (1991), p. 29.
6. V. N. Borshch, E. V. Pugacheva, S. Ya. Zhuk, et al., "Multi-component metallic catalysts of deep oxidation of carbon monoxide and hydrocarbons," *Dokl. Akad. Nauk*, **419**(6), 775 – 777 (2008).
7. M. V. Tsodikov, V. V. Teplyakov, A. S. Fedotov, et al., "Study of the structure of nanosize porous membrane-catalytic systems, high-activity in processes of carbon dioxide conversion of biomass reprocessing products," *Izv. Akad. Nauk, Ser. Khim.*, No. 12, 128 – 155 (2011).
8. M. Koidzumi (ed.), *The Chemistry of Synthesis by Combustion* [Russian translation], Mir, Moscow (1998).
9. K. K. Strelov, *Theoretical Principles of Refractory Materials Technology* [in Russian], Metallurgiya, Moscow (1985).
10. M. M. Martynyuk, P. A. Tamanga, and N. Yu. Kravchenko, "Phase diagram of titanium near a liquid–vapor phase transition," *Vestn. RUDN, Ser. Fiz.*, No. 10, Issue 1, 121 – 125 (2002).
11. A. N. Ivanov, *Hydrodynamics of Developed Cavitation Flows* [Russian translation], Mir, Leningrad (1980).
12. V. I. Moskvitin, I. V. Nikolaev, and B. A. Fomin, *Metallurgy of Light Metals* [in Russian], Intermet Inzhiniring, Moscow (2005).
13. V. S. Bakunov, V. L. Balkevich, I. Ya. Guzman, et al., *Practical Course on the Technology of Ceramics and Refractories* [in Russian], Stroizdat, Moscow (1972).
14. A. P. Babichev, N. A. Babushkina, and A. M. Bratkovskii, *Handbook of Physical Quantities* [in Russian], Énergoatom, Moscow (1991).
15. L. V. Gurvich, I. V. Veits, V. A. Medvedev, et al., *Thermodynamic Properties of Individual Substances* [in Russian], Nauka, Moscow (1978 – 1982), Vols. 1 – 4.